

$^{69,71}\text{Ga}$ NMR studies of a superconducting Ga_{84} cluster compound

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Abstract. We present $^{69,71}\text{Ga}$ -NMR experiments on microcrystalline samples of the recently discovered supramolecular compound $\text{Ga}_{84}[\text{N}(\text{SiMe}_3)_2]_{20}\text{Li}_6\text{Br}_2(\text{thf})_{20}\cdot 2\text{toluene}$, which is composed of ligand-coordinated Ga_{84} metal clusters, packed together in a fully ordered crystalline matrix. The compound is highly conducting and even shows superconductivity below $T_c \sim 7.2$ K. Our preliminary results between 10–300 K show a metallic-like behavior: the nuclear spin-lattice relaxation rate T_1^{-1} follows the Korringa law $^{69}(T_1 T)^{-1} = 0.36 \text{ s}^{-1}\text{K}^{-1}$, but with a relaxation rate approximately three times smaller than in bulk α -Ga metal. No quantum-size effects are observed, the Korringa law being followed down to 10 K, whereas the quantum-gaps for individual clusters should amount to $\sim 10^3$ K. These results therefore suggest a transport process based on intermolecular charge transfer, similar as in alkali-doped fullerenes and silicon-clathrates.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 71.28.+d Narrow-band systems; intermediate-valence solids – 74.70.-b Superconducting materials – 76.60.-k Nuclear magnetic resonance and relaxation

1 Introduction

Recently, $\text{Ga}_{84}[\text{N}(\text{SiMe}_3)_2]_{20}\text{Li}_6\text{Br}_2(\text{thf})_{20}\cdot 2\text{toluene}$, a novel supra-molecular compound built up of Ga_{84} metal clusters directly bonded by twenty $\text{R} = \text{N}(\text{SiMe}_3)_2$ ligands (*cf.* Fig. 1) has been synthesized [1]. The giant $[\text{Ga}_{84}\text{R}_{20}]^{4-}$ cluster molecules shown in Figure 1 form a fully ordered ionic crystal together with the $\text{Li}_6\text{Br}_2(\text{thf})_{20}$ counter-ions ($2\text{Li}(\text{thf})_4^+$, $2\text{Li}_2\text{Br}(\text{thf})_6^+$). The compound is found to be highly conducting, and recent resistivity and magnetic measurements [2] even showed a type II superconducting transition at $T_c \sim 7.2$ K, with a critical field of about 14 T.

So far these results were interpreted in terms of individual superconducting Ga_{84} clusters, mutually coupled to sufficient extent by weak Josephson junctions to produce bulk superconductivity, similar as in a granular superconductor [2]. However, such a scenario does not explain the high conductivity in the normal phase, nor the high value of T_c as compared to $T_c \sim 1.1$ K for normal (α -phase) bulk Ga. Although Ga may exist in different structural forms, as there are the β -, γ - and δ -Ga phases, which have much higher superconducting T_c values, *i.e.* $T_c \sim 6$ K, 7.6 K and 7.8 K, resp., all these phases are metastable at room temperature and are only formed well

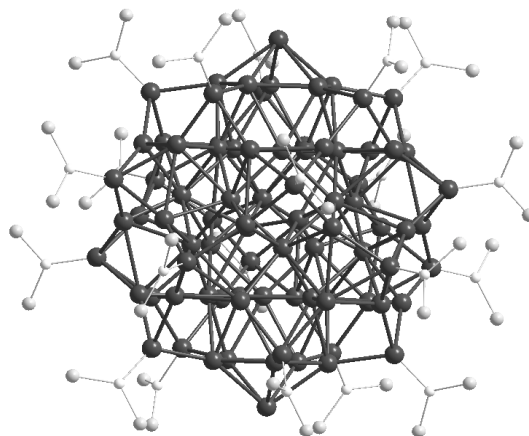


Fig. 1. Molecular structure of the $[\text{Ga}_{84}[\text{N}(\text{SiMe}_3)_2]_{20}]^{4-}$ ion (the $\text{Me} = \text{CH}_3$ groups are not shown).

below 0 °C. Since the cluster compound is synthesized at 50 °C, it is very unlikely that particles of these phases could have been formed as inclusions. Furthermore, if the Ga valence electrons would be confined to a particle as small as 84 Ga atoms, quantum-size effects would lead to an average splitting of about 10^3 K of the electronic levels. Since this is much higher than the condensation energy of a superconductor with $T_c \sim 7.2$ K, the individual

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particles are not expected to show any superconductivity at all. Alternative explanations, such as molecular superconductivity similar as in the alkali-doped fullerenes and silicon-clathrates [3,4] should therefore not be ruled out.

In an attempt to clarify the situation we have started $^{69,71}\text{Ga}$ -NMR experiments on microcrystalline samples. Our preliminary results show a metallic-like behavior: the nuclear spin-lattice relaxation rate T_1^{-1} follows the Korringa law $(^{69}T_1T)^{-1} = 0.36 \text{ s}^{-1}\text{K}^{-1}$, but with a relaxation rate approximately three times smaller than in bulk α -Ga metal [5]. No quantum-size effects are observed, the Korringa law being followed down to 10 K. Calibration of the Ga NMR signal with an Al reference sample shows that the concentration of Ga nuclei observed is as expected from the chemical formula. These results would agree with a transport process similar as found for organic (super)conductors. Low magnetic field measurements to probe the superconductivity are in preparation.

2 Experiment and analysis

The nuclear spin-lattice relaxation time T_1 was measured by standard pulse-NMR techniques in a home-built spectrometer with an applied magnetic field $B = 4.7 \text{ T}$. The NMR lineshape was recorded by measuring the integrated intensity of the spin-echo as a function of frequency. Typical $\pi/2$ pulse lengths were 10 ms. For comparative purposes, data on a polycrystalline bulk Ga sample were taken at room temperature. We first summarize the known magnetic resonance data for bulk Ga. Literature values [6] for the NMR frequencies in $B = 1 \text{ T}$ for the two isotopes ^{69}Ga and ^{71}Ga are 10.22 and 12.984 MHz, respectively. Both isotopes have a nuclear spin $I = 3/2$, the cited electric quadrupole moments [6] are 0.178 and 0.112 barn, respectively. Nuclear quadrupole resonances were found to be 10.908 and 6.866 MHz, respectively [7] at 0°C . (Their ratio is given by that of the quadrupole moments.)

In a previous study of the nuclear spin-lattice relaxation time in bulk Ga metal by Hammond *et al.* [5], particles of about 2 to 3 μm were involved. For a free-electron type metal like Ga, one expects the relaxation to display the Korringa-law: $1/T_1T = A^2(T)(\mathbf{I} \cdot \mathbf{s})\rho^2(E_F)$ where I and s are the spins of the nucleus and the conduction electrons, respectively, and $\rho(E_F)$ is the density of electronic states at the Fermi surface. This relation was found [5] to hold approximately, the product T_1T being about 1.01 sK below $T = 4.2 \text{ K}$, gradually decreasing above 40 K to a value of 0.73 sK at 300 K. These quoted results are for ^{69}Ga , the data for ^{71}Ga were mentioned to be similar. The ratio of the T_1 's for both isotopes were found to be given by the squared ratio of their nuclear magnetic moments, proving that the relaxation process is indeed arising from the magnetic hyperfine interaction. The origin of the slight temperature dependence remained unclear, although some suggestions were made. No details on the lineshapes were given [5].

In Figure 2 we show our own measurement of the bulk ^{69}Ga line at $T = 300 \text{ K}$ in 4.7 T. The resonance frequency is found at 48.223 MHz, in agreement with the above

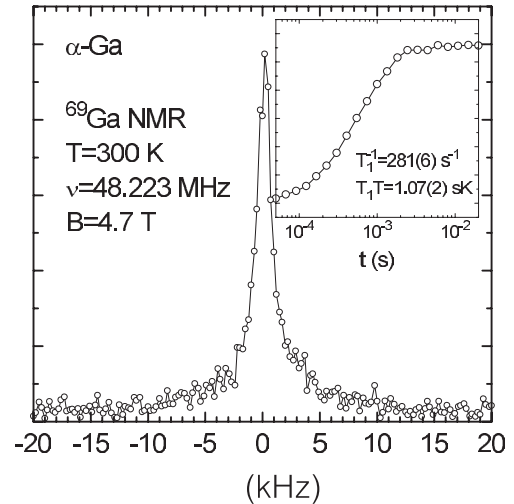


Fig. 2. ^{69}Ga -NMR lineshape measured for bulk α -Ga at $T = 300 \text{ K}$ in $B = 4.7 \text{ T}$. The center of the line is at 48.223 MHz.

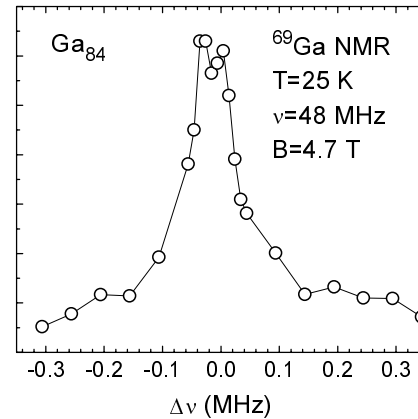


Fig. 3. ^{69}Ga -NMR lineshape found for the Ga_{84} cluster compound at $T = 25 \text{ K}$ and $B = 4.7 \text{ T}$. The center of the line is at 48.0 MHz.

quoted value. The FWHM (full width at half maximum) is about 2 kHz, in accord with the linewidths reported for the NQR lines [7]. The analysis of the recovery, shown in the inset of the figure, yields the value $T_1 = 3.56 \text{ ms}$ and thus $T_1T = 1.07 \text{ sK}$, that is basically the same as the low-temperature result of reference [5].

By contrast our ^{69}Ga -NMR spectra measured for the Ga_{84} cluster compound are characterized by strongly broadened lines, as shown by the example at $T = 25 \text{ K}$ in Figure 3. Considerable structure can be seen, with a peak with FWHM of 100 kHz, superimposed on a much broader background. It should be pointed out that meaningful determinations were restricted to the temperature range below 150 K, as a consequence of the presence of additional nuclear relaxation processes at higher temperatures. The latter can be attributed to hindered molecular rotations, most probably involving the methyl groups present in the R-ligands surrounding the metal cores of the cluster molecules. Such relaxation effects are often found in NMR studies of molecular solids, as for instance in the organic (super)conductors.

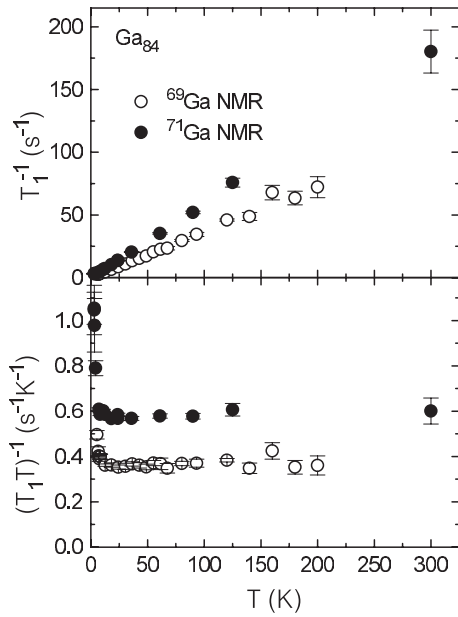


Fig. 4. $1/T_1$ (upper panel) and $1/T_1T$ (lower panel) *versus* T for the Ga_{84} cluster compound. Open and closed symbols refer to ^{69}Ga - and ^{71}Ga -NMR signals, resp.

The nuclear spin-lattice relaxation times associated with the center of the line are plotted in Figure 4 as T_1 and T_1T *versus* the temperature. One may notice that the Korringa relation is well obeyed for both isotopes over the whole temperature range down to about 10 K, below which the products T_1T are seen to speed up. The ratio of the T_1 's for both isotopes is again about 1.60, in accord with the squared ratio of the nuclear magnetic moments. However, the values of the products T_1T are about three times larger than for the bulk metal, *i.e.* for ^{69}Ga we obtain the value 2.8 sK. In order to check whether the signals observed are associated indeed with the Ga atoms present in the cluster molecules, we performed a calibration of the Ga NMR signal with an Al reference. This showed that the concentration of Ga nuclei observed is as expected on basis of the chemical formula of the cluster compound, in agreement with the X-ray analyses in which no traces of other Ga compounds or Ga phases could be detected.

3 Discussion

The observed behavior of the NMR signals is qualitatively similar in several respects to that observed in charge-transfer salts and organic superconductors. This holds in particular for the simultaneous presence of the itinerant electron relaxation channel and the relaxation in the higher temperature range due to molecular rotations. But also the upturn of the product T_1T at the lowest temperatures upon approaching the superconducting region is a phenomenon often seen in organic superconductors. Possible explanations proposed include triplet superconductivity, spin-density wave and vortex lattice melting transitions. Since the present experiment was limited to

a single (and rather high) field value, and to temperatures above T_c ($B = 0$), we cannot comment any further on this point. Measurements at lower temperatures and lower fields are in preparation. However, we mention that foreign magnetic impurities as an additional possible source for nuclear relaxation at low temperatures are ruled out, since low-field magnetic susceptibility studies in the range 2–20 K made on our sample did not show any Curie-type contribution (that would be expected from unpaired spins).

Restricting to the region above 10 K, our results agree with a model involving Ga atoms arranged in ligand-coordinated clusters (so that the nuclei interact with the rotations in the molecular ligand-shells), with sufficient inter-cluster charge-transfer to produce itinerant electron behavior (Korringa-law) throughout the entire supra-molecular crystal. Although this scenario would resemble that of a system of weakly interacting metallic particles, it should be emphasized once more that the Ga clusters involved are so small that the familiar metallic properties will be completely suppressed due to strong quantum size effects. Gallium has only three valence electrons, the electronic configuration is $4s^24p^1$, implying that a cluster of 84 Ga atoms will contain only 126 occupied electron orbitals. Since the energy range spanned by these will be of the order of the bulk Fermi energy, which is $E_F \sim 11$ eV, it follows that the average splitting of the energy levels is about 10^3 K! Clearly, single, mutually isolated Ga_{84} clusters cannot display metallic behavior even at room temperature. However, since the cluster molecules are all identical and are regularly packed into a molecular crystalline array, one may draw a parallel with the situation in alkali-doped crystals of C_{60} molecules. For individual C_{60} molecules the discrete molecular levels are similarly separated by large energy splittings (about 1 eV). By intermolecular charge transfer, however, band motion in the ordered array of clusters becomes possible and each molecular level is transformed into a narrow band of width ~ 0.5 eV given by the strength of the intercluster transfer integral. In undoped C_{60} , the HOMO-level derived band is full, the HOMO-LUMO gap is about 2 eV, so it is an insulator. Doping with alkali-atoms, however, leads to partial filling of the LUMO-derived band, by which conductivity becomes possible and, under suitable levels of doping, even superconductivity at elevated temperatures. A similar qualitative picture applies to Na/Ba-doped silicon clathrate compounds [8,9] and to the charge transfer salts, and we could speculate it to describe the situation in the present molecular crystal as well. Since the product T_1T is inversely proportional to the square of the density of states at the Fermi energy, the latter is a factor of 1.4 smaller than in bulk Ga metal.

The source of the intrinsic doping mechanism in the present compound could be sought in a possible non-stoichiometry of its components, *e.g.* in the exact amount of toluene molecules required by the chemical formula. Another possibility would be the occurrence of a partial disproportionation of the tetravalent $[\text{Ga}_{84}\text{R}_{20}]^{4-}$ cluster molecules into the tri- and pentavalent species. Further

experiments, in particular attempts to vary the degree of such doping mechanisms on purpose, are planned for to further elucidate these remaining questions. We end by pointing out that to our knowledge the here-investigated material is the first example of a metal cluster compound to show metallic conductivity. In previous publications from our group at Leiden [10–12], inter-cluster charge-transfer processes were discussed in terms of the extended Hubbard Hamiltonian. The possible occurrence of metallic conductivity in metal cluster compounds was also discussed on basis of the Kronig-Penney model applied to mesoscopic units, and the analogy with the doped fullerenes was pointed out. However, up till now all crystalline molecular metal cluster compounds known proved to have full-shell electronic structures and did not allow chemical doping.

It is instructive to compare the behavior found for the present cluster compound with our previous ^{195}Pt -NMR studies on the metal cluster compound $\text{Pt}_{309}\text{Phen}_{36}^*\text{O}_{30}$ [13,14]. In that material the Pt_{309} clusters are not ordered in a crystalline array, but are packed randomly, as in a glass. Intercluster charge transfer is very small since the cluster molecules are neutral and thus bonded only by van der Waals forces. Consequently, the valence electrons of the Pt atoms are basically confined to the individual Pt_{309} cluster. However, since each cluster contains about 3×10^3 valence electrons (and $E_F \sim 6$ eV) the quantum gaps due to the finite cluster size are now of the order of 40 K only. Indeed, experimentally the T_1T product was found to follow the Korringa law for temperatures above ~ 50 K, the metallic like behavior arising in this case from the electrons within each individual cluster (the thermal energy and the electron exchange between neighboring clusters only lead to broadening of the cluster energy levels). For lower temperatures deviations from the Korringa law were found, that should be explained in terms of the presence of the quantum gap at E_F .

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